

The Influence of Surface Characteristics on the Performance of Coconut Fiber-Polyester Composites from Recycled Polyethylene Terephthalate

Nurul Munirah Abdullah¹ and Ishak Ahmad²

¹ Department of Chemical and Food Technology, Politeknik Pagoh Johor
d/a : Politeknik Sultan Haji Ahmad Shah, Semambu, 25350 Kuantan. Pahang Darul Makmur.

² School of Chemical Science and Food Technology, Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor.

ARTICLE INFO

Article history:

Received : June 2015

Accepted : August 2015

Available online : January 2017

Keywords:

Adhesion,

ABSTRACT

Unsaturated polyester resin (UPR) based on the glycolized poly(ethylene terephthalate) (PET) with ethylene glycol was prepared through glycolysis process and was used as a matrix for the preparation of UPR/coconut fiber (CF) composites. The oligomer obtained was analyzed according to their molecular weight. To improve the adhesion between coconut fiber and polyester resin, surface treatment on coconut fiber with sodium hydroxide solution (NaOH) and silane coupling agent were used. The effect of fiber surface treatment on mechanical properties of coconut fiber reinforced unsaturated polyester composites were determined by using tensile and impact test. The experimental results showed that treated coconut fibers have higher values of tensile strength and impact strength compared to untreated coconut fiber. Silane treatment on alkalinized coconut fiber shows the highest improvement of tensile strength followed by alkali treated fiber with the increase in tensile strength by 41% and 34% respectively. From SEM observations, better adhesion was observed for the coconut fiber/unsaturated polyester composites in the presence of silane coupling agent on the alkalinized fiber.

1. Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester widely used in application such as textile fibers, films and molded products. Among all plastics, PET has received particular attention in terms of post-consumer recycling due to the relatively large availability of PET bottles from special collection schemes [1]. PET does not create any direct hazard to the environment, but due to the increasing in the plastics waste and its high

resistance to the atmosphere and biological agents, it could be considered as a pollutant material. Therefore, recycling of PET will not only serve as a partial solution to the solid waste problem but also contribute to the conservation of raw petrochemical products and energy. In other words, product made from recycled plastics can result in 50-60% energy saving [2]. PET glycolysis products were hydroxyl-containing oligoester which is bis(2-hydroxyethyl) terephthalate (BHET) and higher monomer. They were usually used for the synthesis of polyester polyols and unsaturated maleic or fumaric polyester resins [3].

Natural fibers are very attractive for composite materials because of their low cost, eco-friendly, available in high quantities, renewable, biodegradable, have excellent mechanical properties and low density [4]. However, the use of natural fibers as reinforcement agent, particularly in hydrophobic polymeric matrices has some drawbacks such as poor adhesion in the fiber/matrix interfacial region. This is because the natural fibers are highly polar due to the high polysaccharide content (hemicelluloses and cellulose), making the lignocellulosic fibers to also be highly hydrophilic [5]. Moreover, the large moisture sorption of natural fibers adversely affects adhesion with hydrophobic matrices that may cause material degradation and loss of strength [6]. Despite the fact that the natural fibers have some disadvantages, it can be solved via various fiber-matrix interface modifications that can improve performance of the resulting composite [7].

In this research, coconut fiber (CF) has been used as fibrous reinforcement in unsaturated polyester resin (UPR) synthesized from glycolyzed product of waste PET. The objective of this study is to analyze the three most used treatments on natural fibers: alkali, silane and silane on alkalinized CF treatment in preparation of UPR/CF composites based on recycled PET. CF surface morphology and fracture surfaces of untreated, alkali treated and silane treated on alkalinized CF composites were investigated by scanning electron microscope (SEM) providing the information for the evaluating of interfacial fiber-matrix adhesion.

2. Experimental

2.1 Materials

White colored drinking bottles of PET were collected from garbage collector, washed, cut and then grounded into fine pieces. Glycolysis of PET was done together with ethylene glycol and zinc acetate. Both chemicals were supplied by MERCH and Riedel-de Haën. Maleic anhydride, hydroquinone and styrene monomer from MERCK were used for the

synthesis of unsaturated polyester resin. Curing process of UPR was done by using Methyl ethyl ketone peroxide (MEKPO) as accelerator and Cobalt octoate as an initiator respectively supplied by Revertex Sdn. Bhd. and Aldrich Co. The coconut fibers that act as a reinforcing agent were obtained from Fibromat (M) Sdn. Bhd. To modified the surface of CF by chemical treatment, Sodium hydroxide (SYSTEM) and silane (Supplied by Dow Corning) were used.

2.2 Preparation of unsaturated polyester resin

Fine pieces of PET were put into a four-necked flat bottom flask with the capacity of 1 L. Ethylene glycol was added into the flask at the ratio of PET:EG = 1:4 (w/w) together with 0.5% zinc acetate based on weight of PET as a catalyst. Then, magnetic stirrer was put into the flask to ensure the mixture occur uniformly. This was carried out under reflux in nitrogen atmosphere with temperature at 190°C for 8 h by using heated silicon oil.

Unsaturated polyester resin (UPR) was prepared by using polyesterification reaction. Glycolysed product from glycolysis reaction was reacted with maleic anhydride at a fixed ratio of 1:1 for the hydroxyl to carboxyl groups. The polyesterification was carried out in a 1 L four-necked round bottom flask connected to a reflux condenser under nitrogen gas at 200°C. The experiment was done by heating the reactant in an oil bath. The acid value was monitored during the reaction and determined by the titration of 0.1 N NaOH into the weighed resin in 100 ml acetone according to ASTM D 1639-90 method. The reaction was stopped when the acid value reached 29-34 mg of KOH/g. The liquid resin was then cooled to 120°C and 0.45% hydroquinone based on weight PET was added to prevent the precuring of the resin. Finally, the liquid resin was dissolved in styrene monomer to achieve a 40% w/w styrene in the resin that equals to commercial UPR [8].

2.3 Fiber treatments

CF in the form of unwoven mat was cut according to the size wanted. Before specific treatments were carried out, the fiber was first rinsed with distilled water to remove the dirt on the fiber surface. Washed CF was left to dry at room temperature and finally dried in oven for 2 hours at 60°C.

2.3.1 Alkali treatments

CF has been treated with 5% (w/v) concentration of alkali. The fiber was immersed in alkaline solution for 2 hours then neutralized with acetic acid and washed with distilled water repeatedly until all sodium hydroxide was eliminated. Finally, the fiber was washed with distilled water and dried at room temperature for 48 h [9].

2.3.2 Silane treatments

CF surface was treated with silane by soaking the fiber in a silane solution of 0.5% (w/v). Silane was firstly dilute with distilled water and stirred using a glass rod for 15 minutes to form an aqueous solution. The silane solution was then added with acetic acid until pH of solution becomes 4 in order to optimize the performance of reinforcing material. CF was immersed in the solution for an hour. Finally, the fiber was washed with distilled water and dried at room temperature for 2 days.

2.3.3 Silane treatment on the Alkalized fiber

CF that has been pretreated with 5% (w/v) alkali solution was immersed in 0.5% (w/v) dilute silane solution using the same method as mentioned before.

2.4 Preparation of composite

In order to prepare CF mat/polyester composites, modification on the CF has been done to get a uniformed thickness of fiber mat. CF in the tangled form [Fig. 1(a)] was vacuumed and compressed with a thickness around ~1-2 mm. CF in the form of unwoven mat was cut according to the size wanted. Washed CF was left to dry at room temperature and finally dried in an oven for 2 hours at 80°C as shown in Fig. 1(b). These fiber mats were used for the preparation of untreated and treated fiber composites. Hand lay-up method was applied. A stainless steel mold with the dimensions of (235 x 235 x 235) mm³ and 3 mm of thickness was used. The curing of the polyester resin was done by the incorporation of 0.75 wt.% cobalt octoate and 1.5 wt.% methyl ethyl ketone peroxide (MEKPO) as a initiator and accelerator respectively. The mixture was then poured on the mat form of CF. The volume fraction of CF in the composite, V_f , was approximately 0.30 with the thickness of specimens was 3 mm. The composite was cured at room temperature for 24 h before removing it from the mold. Finally, the composite was post cured in the oven at 60°C for 6 h.



Fig. 1. Aspect of the coconut fibers: (a) tangled fibers and (b) pressed mat.

2.5 Analysis and testing

The molecular weight of the glycolyzed product and prepared resin were measured by Waters Gel Permeation Chromatography (GPC). All samples were dissolved in tetrahydrofuran (THF) of HPLC grade at the constant concentration 0.1 wt. %.

Tensile test on composites were determined according to ASTM D-638-91 standard. The measurements were done using Instron universal tensile machine (Model 5567) at a speed of 5 mm/min at room temperature.

The impact test was carried out using Universal Fractoscope (CEAST) 6546/000 impact tester according to ASTM D256-88 at room temperature. It was used to test the strength of composite samples when the load was suddenly applied. At least 7 samples were tested for each mechanical measurement.

The scanning electron micrograph of fracture surfaces following the tensile test of composite materials was taken using scanning electron microscope (SEM), Philips XL30. The samples were first dried in oven to remove air moisture and then coated with a thin layer of gold by using Sputter Coater machine. Examination of microscopy has been done at 500X magnification with the highest voltage of 20 V.

3. Results and discussions

3.1 Characterization of glycolyzed product and prepared resin

Results on the average molecular weights of glycolyzed product (BHET) and unsaturated polyester resin (UPR) from recycled PET (UPR-PET) are presented in Table 1. In

this table, results are included on the number average molecular weight (Mn), weight average molecular weight (Mw) and the polydispersity of the molecular weight distribution from the GPC analysis. The alcoholysis consist of the transesterification of PET and the destruction of its molecular chain, resulting in the decrease of its molecular weight. Using glycol in the depolymerization of PET makes the oligoesters obtained have two hydroxyl end groups whereas oligoester diols are formed. The polydispersity of the molecular weight distribution, which was always greater than 1, revealed that the distribution was not unimodal [10]. Furthermore, it can be seen from Table 1 that value of Mw for UPR-PET is nearly same to the value of Mw for commercial resin (1812 g/mol) [8].

Table 1 Molecular weight distribution of BHET and prepared resin.

Sample	Mn (D)	Mw (D)	Polydispersity
BHET	109	112	1.03
UPR-PET	628	1434	2.28

3.2 Tensile test

Fig. 2 shows the analysis results of tensile strength for untreated CF and treated CF composites. It can be seen that the tensile strength increased with the treatment. The increase in tensile strength indicates that modifying the surface of CF improved the interfacial adhesion between CF and polyester matrix. On the other hand, untreated fiber composite has the lowest tensile strength is due to the weak compatibility between fiber and matrix as shown in SEM micrograph of untreated fiber composite in Fig. 3(a). Tensile strength increased 34% for alkali treatment in comparison to the untreated CF composites. This is an indication that alkali treatment improves the fiber-matrix adhesion because of the removal of natural and artificial impurities [Fig. 3(b)]. Moreover, during the alkali treatment, NaOH reacts with hydroxyl groups of the cementing material hemicelluloses and it leads to the destruction of the cellular structure and therefore the fibers splits into filaments. This phenomenon is called fibrillation, which breaks the untreated fiber bundle down into smaller fibrils by the dissolution of the hemicelluloses. This fibrillation then increases the effective surface area available for contact with the matrix. In addition, alkali treatment reduces fiber diameter and thereby increases the aspect ratio, improving mechanical characteristics of the resulting composites [11].

Silane treatment on the surface of CF also increases the tensile strength of the composite with the improvement in the tensile strength is 28%. Silane is a chemical compound with the chemical formula of SiH_4 . Silane is used as coupling agents to allow natural fiber to adhere to a polymer matrix, thus stabilizing the composite material. Silane coupling agents may reduce the number of cellulose hydroxyl groups in the fiber-matrix interface. Silane can be hydrolyzed into silanol when it reacts with moisture in the fiber. This silanol groups reacts with the hydroxyl groups on the surface of fiber, forming a stable covalent bonds on the cell wall. Meanwhile, the remaining silanol groups are adequate of hydrogen bonding or condensing with adjacent silanol groups ($\text{Si} - \text{O} - \text{Si}$). Therefore, the hydrocarbon chain of polymerized silane can adhere to the matrix mainly because of the van der Waals type of attractive forces. As a result, silane-coupling agent forms a bridge at the interface and improves the adhesion between fiber and matrix as like SEM micrograph of silane composite in Fig. 3(c) [12].

However, chemical modification of fiber surface with only alkali or silane treatment was not enough to increase the strength of composite materials. Further treatment with a silane coupling agent solution to provide improvement adhesion between fiber and matrix by chemical interaction was necessary. The improvement of tensile strength for silane treated on alkalized CF composites is higher than that untreated CF composites with a 41% increase. The increase in tensile strength of the silane treatment on alkalized CF composites is due to the improvement of adhesion between the CF and thermoset matrix [Fig. 3(d)]. Moreover, due to the intra and interfibrillar swelling of alkali treatment during first step of pretreatment and the present of covalent bonds between the fiber and matrix after the silane treatment, composites treated with silane on alkalized CF have the highest improvement in the mechanical performance [13].

The tensile strain of CF/UPR composite as a function of variation fiber surface treatment is shown in Fig. 4. It can be seen that untreated CF composite has the lowest tensile strain in comparison to all treated CF composites. Based on Fig. 4, silane treated on alkalized CF composite gave the highest value of tensile strain with the optimum concentration. It can be noted that composites reinforced by silane on alkalized CF were characterized by a little improvement in their resistance (higher tensile strength). During the reaction of silane treatment on alkalized CF, silanol forming stable covalent bond grafted between the microfibrils and leading to a high increase in the tensile strain. It is suggested that by providing additional sites of mechanical interlocking, silane treatment on alkalized CF leads to the improvement of the CF/UPR composites [14].

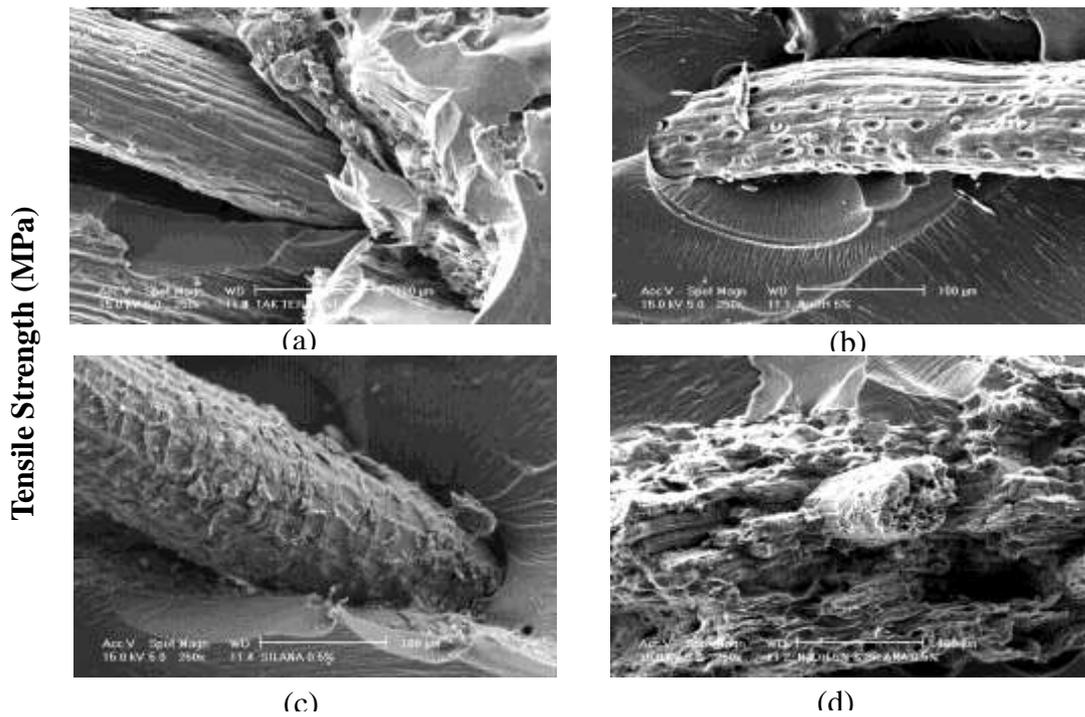


Fig. 2. Tensile strength graph for untreated and treated CF/UPR composites.

Fig. 3. SEM micrographs of tensile fracture surface for the (a) untreated CF composite, (b) alkali treated CF composite, (c) silane treated CF composite, and (d) silane treated on alkalized CF composite.

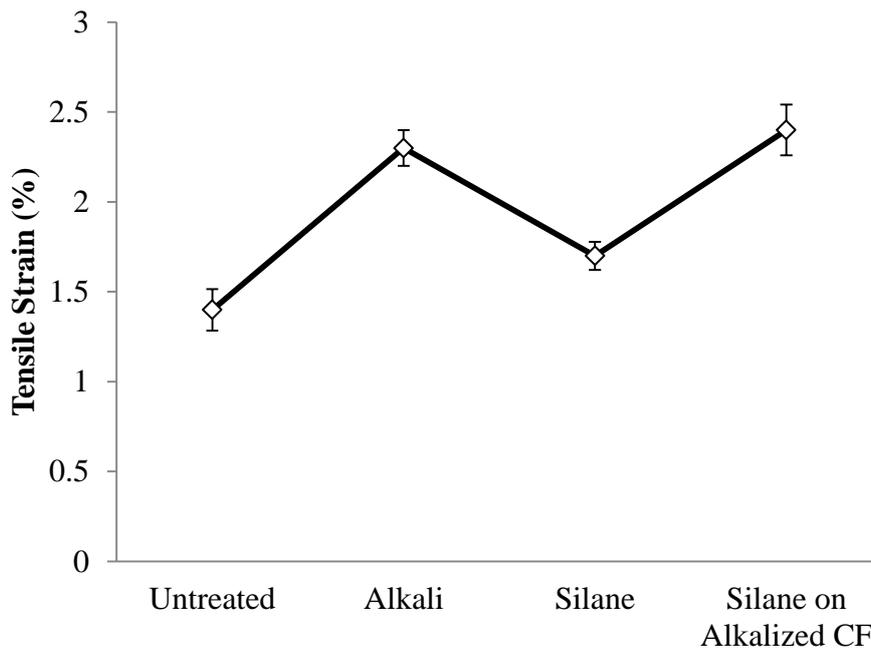


Fig. 4. Tensile strain graph for untreated and treated CF/UPR composites.

3.3 Impact test

Fig. 5 shows the impact strength of CF/UPR composites with variation of fiber surface treatment. Relative to the untreated CF composite, the value of treated CF composites are higher. These results suggest that the treatment had improved adhesion between the CF and UPR matrix and can act to prevent the propagation of cracks generated during the impact test. The fiber/matrix adhesion mainly determines the strength of composites. Improved adhesion after treatment can lead to perfect bonding and thus the failure of composites can occur at relatively high impact strength. Composite having better interfacial bonding need more energy absorbing capacity when the crack propagation occur along the fiber/matrix interface and this is lead to a significant increase of impact strength [15].

The highest amount of impact strength is for silane treated on alkalized CF composites and these are similar to the tensile analysis results. Further treatment with silane coupling agent on alkalized CF has induced chemical interaction between the fiber and the matrix where hydroxyl group on the cellulose fibers could interact better with the silane due to the availability of possible reaction sites in large numbers. Hence, chemical treatment with silane on alkalized CF has increased the mechanical properties of composite from the aspects of tensile and impact strength.

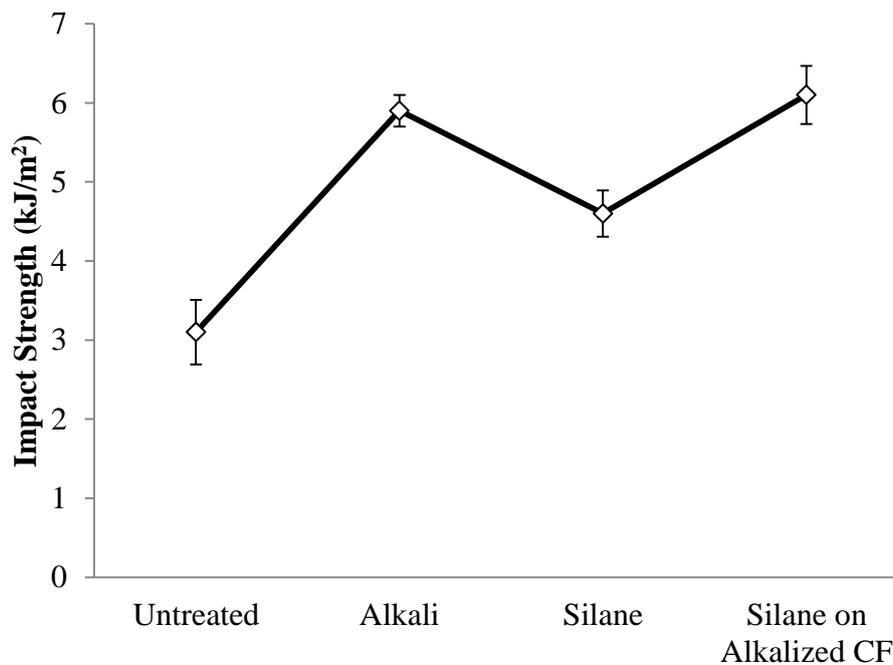


Fig. 5. Impact strength graph for untreated and treated CF/UPR composites.

3.4 Scanning electron microscopy

Scanning electron microscopic analysis examined the surface morphology of treated and untreated CF. The removal of surface impurities on plant fibers is advantageous for fiber-matrix adhesion as it facilitates both mechanical interlocking and the bonding reaction [16]. Fig. 6 shows the SEM images of CF surfaces before and after modification with alkali, silane and silane on alkalinized CF. After the alkali treatment [Fig. 6(b)], the surface of the fiber becomes rougher and micropores were more visible compared to untreated fiber. Alkali treated CF surface showed rough surface topography due to the removal of hemicelluloses, lignin and amorphous waxy layer. Fig. 6(d) shows the SEM micrograph of silane treatment on alkalinized CF surface structure. The surface of the fiber becomes rougher in comparison to untreated fiber and micropores were not so apparent in comparison to alkali treatment and silane treatment. Cellulose is generally unreactive to many chemicals and the OH groups of the microfibrils have very low accessibility. Based on this fact, an optional step is to activate the alkoxy silane by hydrolyzing the alkoxy groups, thereby forming a more reactive silanol groups. As a result, the silanol may react with the hydroxyl groups of fibers and facilitate the enhancement of interfacial adhesion of treated fibers and polymer matrices [17].

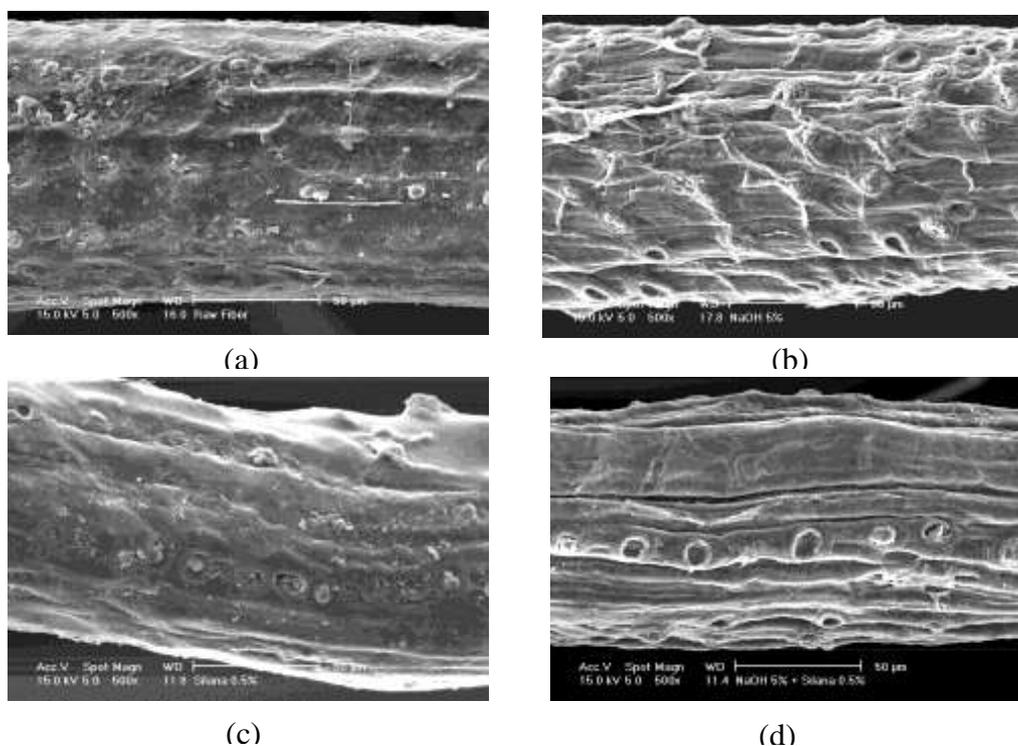


Fig. 6. SEM micrographs of fiber surface for the (a) untreated CF, (b) alkali treated CF, (c) silane treated CF, and (d) silane treated on alkalinized CF.

4. Conclusion

Chemical recycling of waste PET bottles through glycolysis was successfully performed to produce unsaturated polyester resin (UPR) which was suitable to be a matrix for the preparation of composite polyester reinforced coconut fiber. The effect of fiber surface treatment on the mechanical strength coconut fiber/polyester composites have been carried out and treated fiber composites showed better results compared to the untreated fiber composite. For mechanical properties of composites, silane treatment of alkalinized coconut fiber has given the highest mechanical strength compared to other composite samples followed by alkali and silane treatment respectively. From SEM morphology, it was demonstrated that the fiber surface treatments changed the morphology of the fibers; removing cementing materials, creating voids and producing fiber fibrillation. These effects lead to a better adhesion between fiber and matrix.

Acknowledgements

The authors would like to extend their utmost gratitude to the Ministry of Higher Education (MOHE), Malaysia for funding the project under FRGS 06-01-02-SF1017 and for awarding a National Science Fellowship Scholarship to the first author. The authors would also like to acknowledge the Polymer Research Centre (PORCE) of Universiti Kebangsaan Malaysia (UKM) for their support in providing the infrastructure for the project.

References

- [1] Pegoretti, A. & Penati, A. 2004. Recycled Poly(ethylene terephthalate) and Its Short Glass Fibres Composites: Effect of Hygrothermal Aging on the Thermo-Mechanical Behaviour. *Polymer* 45: 7995-8004.
- [2] Suh, D.J., Park, O.O. & Yoon, K.H. 2000. The Properties of Unsaturated polyester Based on the Glycolyzed Poly(ethylene terephthalate) With Various Glycol Compositions. *Polymer* 41: 461-466.
- [3] Radenkov, Ph., Radenkov, M., Grancharov, G. & Troev, K. 2003. Direct Usage of Products of Poly(ethylene terephthalate) glycolysis for Manufacturing of Glass Fibre_reinforced Plastics. *European Polymer Journal* 39: 1223-1228.

- [4] Rozman, H.D., Tan, K.W., Kumar, R.N., Abubakar, A., Mohd. Ishak, Z.A. & Ismail, H. 2000. The Effect of Lignin as a Compatibilizer on the Physical Properties of Coconut Fiber-Polypropylene Composites. *European Polymer Journal* 36: 1483-1494.
- [5] Megiatto Jr, J.D., Silva, C.G., Ramires, E.C. & Frollini, E. 2009. Thermoset Matrix Reinforced With Sisal Fibers: Effect of the Cure Cycle on the Properties of the Biobased Composite. *Polymer Testing* 28: 793-800.
- [6] Bessadok, A., Langevin, D., Gouanve, F., Chappey, C., Roudesli, S. Marais, S. 2009. Study of Water Sorption on Modified Agave Fibres. *Carbohydrate Polymers* 76: 74-85.
- [7] Harish, S., Michael, D.P., Bensely, A., Mohan Lal, D. & Rajadurai, A. 2009. Mechanical Property Evaluation of Natural Fiber Coir Composite. *Material Characterization* 50: 44-49.
- [8] Dayang Ratnasari Abu Bakar, Ishak Ahmad & Anita Ramli. 2006. Chemical Recycling of PET Waste from Soft Drink Bottles to Produce a Thermosetting Polyester Resin. *Malaysian Journal of Chemistry* Vol. 8, No. 1: 022-026.
- [9] Seki, Y. 2009. Innovative Multifunctional Siloxane Treatment of Jute Fiber Surface and Its effect on the Mechanical Properties of Jute/Thermoset Composites. *Materials Science and Engineering A* 508: 247-252.
- [10] Karayannidis, G.P., Achilias, D.S., Sideridou, I.D. & Bikiaris, D.N. 2005. Alkyd Resin Derived from Glycolized Waste Poly(ethylene terephthalate). *European Polymer Journal* 41: 201-210.
- [11] Rosa, M.F., Chiou, B., Medeiros, E.S., Wood, D.F., Williams, T.G., Mattoso, L.H.C., Orts, W.J. & Imam, S.H. 2009. Effect of Fiber Treatments on Tensile and Thermal Properties of Starch/Ethylene Vinyl Alcohol Copolymers/Coir Biocomposites. *Bioresource Technology* 100: 5196-5202.
- [12] Akil, H.M., Omar, M.F., Mazuki, A.A.Z., Safiee, S., Ishak, Z.A.M. & Abu Bakar, A. 2011. Kenaf Fiber reinforced Composites: A Review. *Materials and Design* xx: xx-xx
- [13] Brahmakumar, M., Pavithran, C. & Pillai, R.M. 2005. Coconut Fibre Reinforced Polyethylene Composites: Effect of natural Waxy Surface Layer of The Fibre on Fibre/Matrix Interfacial Bonding and Strength of Composites. *Composites Science and Technology* 65: 563-569.

- [14] Bessadok, A., Roudesli, S., Marais, S., Follain, N. & Lebrun, L. 2009. Alfa Fibres for Unsaturated Polyester Composites Reinforcement: Effect of Chemical Treatments on Mechanical and Permeation Properties. *Composites Part A* 40: 184-195.
- [15] Sreekumar, P.A., Thomas, S.P., Saiter, J.M., Joseph, K., Unnikrishnan, G. Thomas, S. 2009. Effect of Fiber Surface Modification on the Mechanical and Water Absorption Characteristics of Sisal/Polyester Composites Fabricated by Resin Transfer Molding. *Composites Part A* 40: 1777-1784.
- [16] Saw, S.K., Sarkhel, G. & Choudhury, A. 2011. Surface Modification of Coir Fibre Involving Oxidation of Lignins Followed by Reaction With Furfuryl Alcohol: Characterization and Stability. *Applied Surface Science* 257: 3763-3769.
- [17] Xie, Y.J., Hill, C.A.S., Xiao, Z.F., Militz, H. & Mai, C. 2010. Silane Coupling Agents Used for natural Fiber/Polymer Composites: A Review. *Composites Part A* 41(7): 806-819.